X-RAY SPECTROMETRY
*X-Ray Spectrom*. 2000; **29**: 267–278

# PIXE studies of emeralds

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**A total of 56 natural emeralds and 26 synthetic emeralds were studied by PIXE. From the PIXE spectra and the concentrations of 33 elements, i.e. Sc, Ti, V, Cr, Mn, Fe, Ni, K, Rb, Cs, Ca, Sr, Ba, Co, Cu, Zn, Y, Zr, La, Ce, Ga, P, S, Cl, As, Br, Mo, W, Pb, Bi, Pt, Au and Rh, obtained from the bulk analyses of inclusion-free regions of the stones, criteria for differentiating between natural and synthetic emeralds and among different localities of natural emeralds were deduced. The use of concentrations of only three chromophoric elements, Cr, Fe and V, allowed us to attribute Pakistan emeralds, Chatham, Gilson, Taiwan and Lennix flux emeralds and a mixed group incorporating Russian flux and Russian hydrothermal emeralds. We then investigated all 32 elements (Rh was not detected in all the samples) through principal component analysis (PCA), which allowed us to specify whether an emerald was natural or synthetic in the first place and we were then successful in attributing the stone, as a second step, to four localities for natural stones, and to eight types for synthetic stones, one of which was a mixed group. The PCA of a reduced set of six elements, Cr, Fe, V, Mn, Ti and Cl, allowed us to attribute Pakistan emeralds, Taiwan flux emeralds, Biron hydrothermal emeralds and Biron hydrothermal emeralds measured at the boundary, and Lechleitner emeralds. This PCA together with the study of the correlation of the three chromophoric elements, Cr, Fe and V, allowed us to attribute Colombian and Pakistan emeralds and all synthetic emeralds, which was useful and convenient in real-life testing of unknown emeralds. Copyright © 2000 John Wiley & Sons, Ltd.**

## INTRODUCTION

Emerald is the green variety of the mineral beryl with the chemical composition beryllium aluminium silicate, $Be_3Al_2(SiO_3)_6$. Other varieties of beryls include aquamarine, morganite, heliodor, vanadium beryl, red beryl, yellow beryl, violet beryl and colorless beryl. Emerald is allochromatic, with the color of the natural stones arising from the trace concentrations of chromium and vanadium. Gemologists face three tasks in testing emeralds. The first is the judgement of whether an emerald is natural or synthetic. Synthetic emeralds are grown either by the flux method or the hydrothermal method. The second is the determination of the locality if the emerald is natural. The third is the identification of any treatment such as oiling or painting.

There are certain methods in traditional gemology to differentiate between natural and synthetic emeralds, and to differentiate among different localities of natural emeralds. For example, the quickest way is to measure their refractive indices and specific gravities since the ranges of these values are somewhat different. However, a drawback is that there are serious overlaps of values.[1] A UV fluorescence test has also been used. Bright red fluorescence in longwave ultraviolet light may be regarded as a warning that an emerald might be synthetic, but it has also been stated that fluorescence tests are not conclusive.[2] By far the most conclusive results are obtained by the microscopic examination of the inclusions. Nevertheless, it is not uncommon that a piece of emerald is clean or does not have diagnostic inclusions, and no information on inclusions can be obtained from rough stones. Therefore, some quick, accurate and non-destructive techniques are desirable for differentiating between emeralds.

One such technique is based on the examination of the concentrations of certain trace elements in the emeralds. Natural emeralds from different localities are associated with different geologies, while synthetic emeralds from different manufacturers or from different synthetic processes have different ingredients, so it is feasible to identify the origin of the emeralds by examining their trace elements. Previously, relatively comprehensive non-destructive analyses of trace elements in emeralds were carried out using energy-dispersive x-ray fluorescence (EDXRF) and electron microprobe analysis,[3,4] and fruitful results were obtained. In the present work, the technique of micro-proton-induced x-ray emission (micro-PIXE) was employed. Broad-beam PIXE and micro-PIXE techniques have been used previously in the study of rubies.[5–7] Micro-PIXE has the advantage over broad-beam PIXE or EDXRF that it has a scanning power, so it is easy to define an area of any shape on the emerald to avoid the inclusions for irradiation, so that bulk analysis of an inclusion-free region can be obtained. In comparison with electron microprobe analysis, micro-PIXE has much higher sensitivities or much lower limits of detection, and measures properties of the sample to a greater depth which should then be closer to the bulk properties.

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*Received 15 November 1999*
*Accepted 25 April 2000*

## EXPERIMENTAL

### Equipment

The nuclear microscopy facility employed comprised a 2.5 MV Van de Graaff accelerator and a coupled triplet of magnetic quadrupole lenses. The data acquisition system was PC-based and operated under Windows. It allowed a target area of any shape to be defined easily for imaging. Details of the experimental set-up can also be found elsewhere.[8]

Our study involved the use of two techniques simultaneously, namely PIXE and Rutherford backscattering spectroscopy (RBS). The former was employed to obtain the elemental compositions of the specimens and the latter to determine the specimens' matrix composition and estimate the total charge of irradiation (which was related to the beam current and the acquisition time). The total charge of irradiation for individual scans for our experiments varied from 0.03 to 0.1 μC depending on the strength of the signals. The current was kept below 500 pA. The resolution of the beam size was better than 1 μm. An Si(Li) detector of active area 71 $mm^2$ with a 12 μm thick beryllium window was used for x-ray detection and a PIPS detector of 25 $mm^2$ sensitive area was used for counting the backscattered protons.

### Samples

For natural emeralds, we had 20 specimens from Colombia, six from Pakistan, 25 from Zambia and five from Brazil. For synthetic emeralds, we had five Chatham, four Gilson, five Russian, two Taiwan and one Lennix stones which were manufactured using the flux method, and three Biron, five Russian and one Lechleitner stones which were manufactured using the hydrothermal method. Prior to analysis, the samples were cleaned thoroughly with acetone.

The stones were mounted on a layer of Blu-Tack adhered to a copper sample holder of size 4 × 2 cm in such a way that a flat surface of each stone was facing upwards, and all these surfaces of the stones were on the same plane to facilitate the focusing of the proton beam on their surfaces. For stones with emerald cuts, the table facet was chosen as the surface for irradiation; for cabochons, the base was used; and for rough stones, a flat surface was employed. Special care was taken not to contaminate this surface with the Blu-Tack. If it was contaminated, structures would appear on the maps of the elements characteristic of the Blu-Tack. Prior to the measurements, these mounted stones together with the Blu-Tack were coated with a thin layer of carbon to prevent the accumulation of charge on their surfaces during proton bombardment, which would increase the background for the detection of x-ray signals.

### Procedure

Protons of 2 MeV were used for excitation and a Kapton filter of thickness 50 μm was placed between the specimen and the detector to cut down the aluminum and silicon signals in order to enhance the detectability of the heavier trace elements. The typical beam spot size was about 1 μm. In addition to the PIXE and RBS spectra, elemental maps were also recorded for a number of elements of interest, including Si, S, Cl, K, Ca, Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Ga, Rb, Mo, Cs, Pt, Au and Pb. Before each actual run of an emerald sample, data were recorded for a few minutes so that the elemental maps (in particular that of Si) could be examined carefully. A user-defined raster of any shape could be selected for the actual irradiation. The silicon map gave an outline of the emerald so that it was easy to ensure that the irradiation was on the stone itself. The silicon intensities would help identify a flat surface which could be chosen for irradiation; a non-flat surface, such as the incorporation of a tilted facet, would lead to an image with non-uniform silicon intensities. The imaging time for our samples was around 10–20 min, depending on the count rate, but the actual time needed for a routine test may be shorter.

## RESULTS AND DISCUSSION

### PIXE spectra

Typical PIXE spectra for emeralds from different origins are shown in Fig. 1. There are regions of interest (hereafter referred to as channels) which provided information on the origin of the emeralds. The first six channels were Si, Cl, K, Ca, Sc, Ti which were numbered from 1 to 6, respectively. We then came to the three chromophore elements, i.e. V (one channel), Cr (two channels) and Fe (two channels), which were denoted the V, R and I channels, respectively. In some cases, two cesium peaks could be identified between channels 5 and V. In fact, there should also be a third cesium peak at the V channel, but it was masked by the V peak most of the time. On the right half of the spectra, we had channels characteristic of synthetic emeralds, namely Pt (three channels), Au (three channels), Pb (three channels) and Mo (two channels), which were denoted the P, G, L and M channels, respectively. Numerous signals between the second I channel and the first L channel came from pile-ups.

Some criteria for differentiating between natural and synthetic emeralds and for differentiating among different localities of natural emeralds could be obtained by observations of the typical PIXE spectra of the emeralds. The criteria for differentiating between natural and synthetic emeralds are first presented. The first criterion concerns the elements characteristic of the synthetic emeralds, namely Pt, Au, Pb and Mo. If peaks of these elements are identified, the emerald is synthetic. Pt and Au are used for the crucible or for the seed plate for the synthetic growth of emeralds to take place, and oxides of Pb and Mo are used as flux components.[2] The second criterion concerns the V and Cr peaks: if V or/and Cr peaks are very small or absent, the emerald is synthetic. The third criterion concerns the intensity of the Cl peak. If the Cl peak is strong, e.g. Cl ≈ V, Cr(K$\alpha$) for the Biron hydrothermal emerald, the emerald is synthetic. The fourth criterion concerns the relative intensities of the Fe(K$\alpha$), Cr(K$\alpha$) and V peaks. All natural emeralds have Fe(K$\alpha$) > Cr(K$\alpha$) or at least Fe(K$\alpha$) ≈ Cr(K$\alpha$), except for Colombian stones.

 

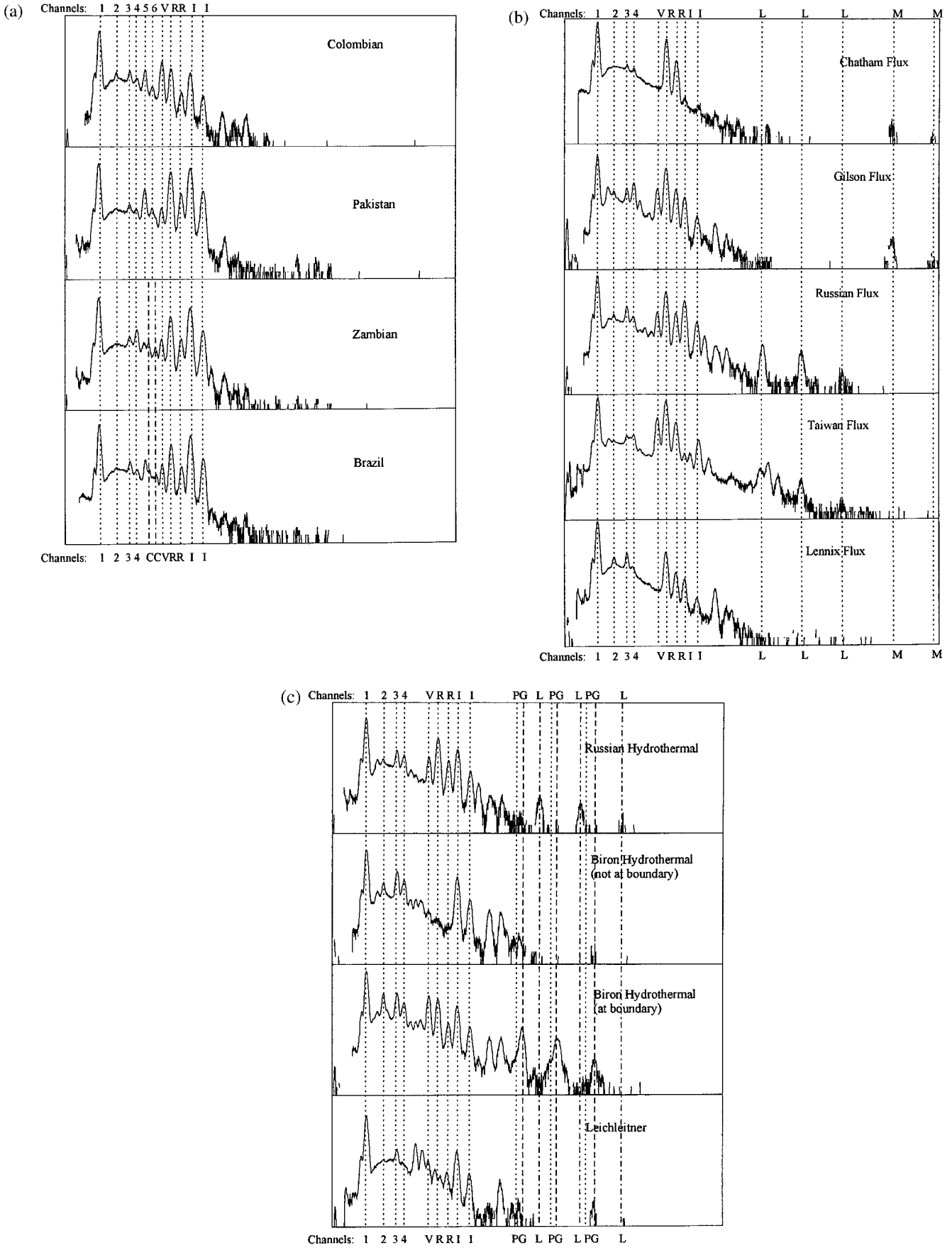


**Figure 1.** Typical spectra of emeralds of different origins: (a) natural, (b) flux grown and (c) hydrothermal grown. Channel codes: 1 = Si, 2 = Cl, 3 = K, 4 = Ca, 5 = Sc, 6 = Ti, C = Cs, V = V, R = Cr, I = Fe, P = Pt, G = Au, L = Pb, M = Mo. Note that the *y*-axis is on a logarithmic scale.

 

Colombian emeralds have Fe(K$\alpha$) < Cr(K$\alpha$), but have strong V peaks with V much higher than Cr(K$\beta$), and even near to or higher than Cr(K$\alpha$) in most cases. All synthetic stones not fulfilling the second and third criteria above have Fe(K$\alpha$) < Cr(K$\alpha$) and at the same time V $\approx$ Cr(K$\beta$) or V < Cr(K$\beta$). We now come to the criteria for differentiating between the localities of natural emeralds. Colombian emeralds are easy to distinguish as just described. Pakistan emeralds do not have conspicuous cesium peaks whereas Brazilian and Zambian stones have. Brazilian and Zambian stones are difficult to separate by observing the PIXE spectra alone.

## Elemental concentrations

The first step in determining the elemental concentrations was to obtain the matrix composition from the RBS spectra using NUSDAN.[9] With this matrix composition, the PIXE spectra could be analysed with the GUPIX code[10] running in the 'trace' mode. The uncertainty of the derived concentrations was estimated to be $\pm$10% from measurements of NBS glass standard (NBS 610).[11] The concentrations of a total of 33 chemical elements were measured, i.e. Sc, Ti, V, Cr, Mn, Fe, Ni, K, Rb, Cs, Ca, Sr, Ba, Co, Cu, Zn, Y, Zr, La, Ce, Ga, P, S, Cl, As, Br, Mo, W, Pb, Bi, Pt, Au and Rh. The results are presented in Tables 1–5. In Table 1, the results for Sc, Ti, V, Cr, Mn, Fe and Ni are shown. These are the transition metals which were used in previous work to differentiate between natural and synthetic emeralds.[1,3,4] In Table 2, the results for the alkali and alkaline earth metals K, Rb, Cs, Ca, Sr and Ba are shown. Table 3 shows the results for miscellaneous elements, which include the transition metals Co, Cu, Zn, Y and Zr, the lanthanides La and Ce and the metal Ga. Table 4 lists the results for the non-metallic elements P, S, Cl, As and Br. Table 5 shows the results for the elements which have previously been thought to be closely related to synthetic stones, including Mo, W, Pb, Bi, Pt and Au. Rh was detected by previous authors[1,4] in synthetic emeralds, and was found[1] to be used as a protective coating for platinum wires used in the crucible during the synthetic growth of the emeralds. However, this was not detected in any of the samples studied in the present work so it is not listed in any of the tables, and will not be included in the statistical analysis part below.

In Tables 1–5, the range of concentrations (in ppm) of the elements of interest are given for different types of emeralds, with zero referring to concentrations below the limit of detection. There is only one sample in each of the Lennix and Lechleitner category, so only single values are reported rather than ranges. It is specially noted that Ce in Table 3 was not measured in previous investigations.[1,3,4] Significant amounts were identified in some of our Colombian emeralds. Similarly, significant amounts of lanthanum were found for these stones. These together indicated that the stones came from the Muzo mine in Colombia, since it is well known that emeralds from this mine may contain crystals of the rare mineral parisite, $Ca(Ce,La)_2(CO_3)_3F_2$.

Most elemental concentrations did not provide criteria for attribution of a natural or synthetic emerald. The few exceptions are described as follows. The presence of Mo and high concentrations of Pb (say >1000 ppm) imply a synthetic nature, which is consistent with part of the first criterion obtained above from PIXE spectra. Although the PIXE spectra of Biron hydrothermal emeralds showed conspicuous Pt and Au peaks at the boundary of the seed crystal, the spectra taken at the boundary were not employed for the analyses for the elemental concentrations, since it is believed that most Biron hydrothermal emeralds in the market will not contain a seed crystal. The absence of V or Cr showed that the emerald is synthetic, which is consistent with the second criterion obtained above from PIXE spectra. The absence of Sc also pointed to a synthetic nature. A rich Cl content (say >5000 ppm) implies a synthetic nature, which is consistent with the third criterion obtained above from PIXE spectra. An Fe content significantly above 10 000 ppm indicates a natural emerald and an Fe content significantly below 10 000 ppm indicates a synthetic or a Colombian stone.

## Comparison among data from different investigations

Up to now, relatively comprehensive analyses of emeralds were presented in Refs 1, 3 and 4. The comparisons of our results with those data are shown in Table 6. The data

**Table 1. Range of concentrations (ppm) of the elements Sc, Ti, V, Cr, Mn, Fe and Ni in different types of emeralds, with zero referring to concentrations below the limits of detection[a]**

| Sample[b] | Sc | Ti | V | Cr | Mn | Fe | Ni |
|---|---|---|---|---|---|---|---|
| Colombian (20) | 205–1436 | 0–115 | 300–8535 | 1046–16862 | 0–124 | 1440–18996 | 0–50 |
| Pakistan (6) | 2075–7951 | 0–219 | 367–1692 | 11753–30399 | 0–0 | 9744–50890 | 16–98 |
| Zambian (25) | 310–3502 | 0–89 | 777–2375 | 3587–15435 | 0–156 | 20060–54309 | 36–402 |
| Brazil (5) | 339–2934 | 0–355 | 1208–1822 | 5362–16244 | 0–189 | 38766–52108 | 62–133 |
| Chatham flux (5) | 0–0 | 0–27 | 0–0 | 15466–19681 | 0–0 | 65–194 | 0–0 |
| Gilson flux (4) | 0–0 | 64–114 | 32–2176 | 8119–17523 | 0–0 | 951–1907 | 23–72 |
| Russian flux (5) | 17–426 | 0–43 | 747–2505 | 7302–11829 | 0–0 | 5557–10480 | 322–746 |
| Taiwan flux (2) | 32–40 | 16–19 | 592–6751 | 35386–52058 | 0–0 | 66–259 | 0–0 |
| Lennix flux (1) | 0 | 15 | 0 | 2933 | 0 | 360 | 0 |
| Biron hydrothermal (3) | 0–0 | 0–292 | 0–11232 | 40–8863 | 0–0 | 0–7812 | 0–31 |
| Russian hydrothermal (5) | 84–399 | 0–83 | 789–1459 | 8675–15036 | 0–0 | 5337–9185 | 408–480 |
| Lechleitner (1) | 49 | 0 | 0 | 0 | 356 | 3442 | 10 |

[a] There is only one sample for each of the Lennix and Lechleitner category, so only single values are reported rather than ranges of values.
[b] The numbers in brackets are the number of samples in the category.

 

**Table 2. Range of concentrations (ppm) of the elements K, Rb, Cs, Ca, Sr and Ba in different types of emeralds, with zero referring to concentrations below the limits of detection[a]**

| Sample[b] | K | Rb | Cs | Ca | Sr | Ba |
|---|---|---|---|---|---|---|
| Colombian (20) | 483–2325 | 0–61 | 0–4320 | 146–2357 | 0–0 | 0–1265 |
| Pakistan (6) | 469–1216 | 0–122 | 689–1516 | 153–1906 | 0–0 | 282–978 |
| Zambian (25) | 673–2283 | 0–120 | 854–3218 | 263–3433 | 0–29 | 0–367 |
| Brazil (5) | 1110–2851 | 0–300 | 1327–6938 | 294–3142 | 0–91 | 0–233 |
| Chatham flux (5) | 210–616 | 0–0 | 0–84 | 193–307 | 0–0 | 0–157 |
| Gilson flux (4) | 1244–1688 | 0–0 | 0–44 | 423–2440 | 0–0 | 0–81 |
| Russian flux (5) | 1040–1926 | 0–159 | 375–937 | 132–383 | 0–0 | 0–0 |
| Taiwan flux (2) | 0–480 | 0 | 162–210 | 334–510 | 0–21 | 166–438 |
| Lennix flux (1) | 1412 | 0 | 0 | 101 | 0 | 44 |
| Biron hydrothermal (3) | 452–5345 | 0–66 | 0–1428 | 48–1772 | 0–0 | 0–281 |
| Russian hydrothermal (5) | 654–1743 | 0–111 | 404–619 | 75–920 | 0–0 | 0–130 |
| Lechleitner (1) | 1316 | 818 | 10923 | 69 | 0 | 0 |

[a,b] See Table 1.

**Table 3. Range of concentrations (ppm) of the elements Co, Cu, Zn, Y, Zr, La, Ce and Ga in different types of emeralds, with zero referring to concentrations below the limits of detection[a]**

| Sample[b] | Co | Cu | Zn | Y | Zr | La | Ce | Ga |
|---|---|---|---|---|---|---|---|---|
| Colombian (20) | 0–110 | 42–1070 | 0–203 | 0–145 | 0–0 | 0–1371 | 0–2335 | 57–243 |
| Pakistan (6) | 0–233 | 0–185 | 20–93 | 0–0 | 0–0 | 0–546 | 0–443 | 17–35 |
| Zambian (25) | 0–262 | 44–329 | 22–212 | 0–100 | 0–98 | 0–474 | 0–509 | 19–273 |
| Brazil (5) | 0–0 | 0–285 | 50–187 | 0–0 | 0–0 | 175–805 | 0–699 | 53–261 |
| Chatham flux (5) | 0–0 | 39–102 | 28–63 | 0–0 | 0–0 | 0–106 | 0–120 | 41–69 |
| Gilson flux (4) | 0–0 | 240–428 | 92–140 | 0–0 | 0–0 | 0–50 | 0–137 | 54–58 |
| Russian flux (5) | 0–0 | 80–1113 | 129–797 | 0–0 | 0–0 | 0–121 | 0–241 | 43–69 |
| Taiwan flux (2) | 0–0 | 0–35 | 0–0 | 0–47 | 0–116 | 171–571 | 144–1248 | 49–64 |
| Lennix flux (1) | 0 | 316 | 67 | 0 | 0 | 0 | 0 | 18 |
| Biron hydrothermal (3) | 0–0 | 98–917 | 19–940 | 0–0 | 0–0 | 0–494 | 0–0 | 0–145 |
| Russian hydrothermal (5) | 0–75 | 48–190 | 112–219 | 0–0 | 0–0 | 0–127 | 0–218 | 20–83 |
| Lechleitner (1) | 0 | 35 | 642 | 0 | 0 | 672 | 0 | 105 |

[a,b] See Table 1.

**Table 4. Range of concentrations (ppm) of the elements P, S, Cl, As and Br in different types of emeralds, with zero referring to concentrations below the limits of detection[a]**

| Sample[b] | P | S | Cl | As | Br |
|---|---|---|---|---|---|
| Colombian (20) | 0–224 | 83–923 | 356–1864 | 0–32 | 0–0 |
| Pakistan (6) | 0–302 | 90–422 | 227–758 | 0–0 | 0–75 |
| Zambian (25) | 0–433 | 0–10707 | 109–1188 | 0–0 | 0–0 |
| Brazil (5) | 0–0 | 175–916 | 351–924 | 0–44 | 0–82 |
| Chatham flux (5) | 0–0 | 184–403 | 110–400 | 0–0 | 0–16 |
| Gilson flux (4) | 0–314 | 541–3982 | 850–1568 | 0–20 | 0–0 |
| Russian flux (5) | 320–1136 | 96–517 | 504–783 | 0–55 | 0–29 |
| Taiwan flux (2) | 1456–2510 | 319–995 | 55–130 | 422–635 | 61–108 |
| Lennix flux (1) | 132 | 102 | 1233 | 0 | 0 |
| Biron hydrothermal (3) | 0–459 | 0–1417 | 2492–11354 | 0–0 | 0–0 |
| Russian hydrothermal (5) | 0–1080 | 0–1425 | 433–706 | 0–40 | 0–0 |
| Lechleitner (1) | 0 | 0 | 209 | 0 | 0 |

[a,b] See Table 1.

from Refs 3 and 4 were originally presented as concentrations of oxides, but were converted to concentrations of the elements for easy comparison with the data in the present work and in Ref. 1. In Table 6, the emeralds are categorized into natural (N), hydrothermal (HT) and flux (F) grown emeralds. Our present data show significantly wider ranges for Cr, Fe and Cl. Possible reasons include (1) we have better sensitivities or lower limits of detection, (2) the localities of the natural stones and/or the manufacturers of the synthetic stones are different and (3) the properties of the stones vary significantly even for a single locality or manufacturer.

 

**Table 5. Range of concentrations (ppm) of the elements Mo, W, Pb, Bi, Pt and Au in different types of emeralds, with zero referring to concentrations below the limits of detection[a]**

| Sample[b] | Mo | W | Pb | Bi | Pt | Au |
|---|---|---|---|---|---|---|
| Colombian (20) | 0–0 | 0–157 | 0–0 | 0–90 | 0–154 | 0–260 |
| Pakistan (6) | 0–0 | 0–0 | 0–86 | 0–58 | 0–66 | 0–96 |
| Zambian (25) | 0–0 | 0–193 | 0–252 | 0–335 | 0–392 | 0–213 |
| Brazil (5) | 0–0 | 0–82 | 0–0 | 0–174 | 0–132 | 0–123 |
| Chatham flux (5) | 98–877 | 0–0 | 0–0 | 0–0 | 0–35 | 0–0 |
| Gilson flux (4) | 0–3394 | 0–0 | 0–46 | 0–65 | 0–0 | 0–0 |
| Russian flux (5) | 0–0 | 0–0 | 0–3135 | 0–89 | 0–75 | 0–0 |
| Taiwan flux (2) | 0–0 | 0–0 | 0–1952 | 0–0 | 365–380 | 128–174 |
| Lennix flux (1) | 0 | 0 | 0 | 0 | 0 | 0 |
| Biron hydrothermal (3) | 0–0 | 0–50 | 0–0 | 0–75 | 0–186 | 0–61 |
| Russian hydrothermal (5) | 0–0 | 0–0 | 0–1823 | 0–0 | 0–0 | 0–0 |
| Lechleitner (1) | 0 | 0 | 0 | 0 | 0 | 0 |

[a,b] See Table 1.

**Table 6. Comparisons of the range of concentrations (wt%) of the elements Ti, V, Cr, Mn, Fe and Cl in different types of emeralds, with zero referring to concentrations below the limits of detection[a]**

| | Origin[b] | Schrader[1] N(44); HT(1); F(13) | Hanni[3] (45 in total) | Stockton[4] N(38); HT(6); F(5) | This work N(56); HT(9); F(17) | This work[c] N(56); HT(4); F(10) |
|---|---|---|---|---|---|---|
| Ti | N | nr | ≤0.06 | nr | ≤0.04 | ≤0.04 |
| | HT | ≤0.013 | nd | nd | ≤0.03 | ≤0.03 |
| | F | nr | nd | nd | ≤0.02 | ≤0.02 |
| V | N | ≥0.005 | ≤0.61 | ≤1.36 | 0.03–0.85 | 0.03–0.85 |
| | HT | 0 | nd | ≤0.48 | ≤1.13 | ≤1.13 |
| | F | 0–0.043 | ≤0.07 | ≤0.07 | ≤0.68 | ≤0.22 |
| Cr | N | ≥0 | ≤0.96 | ≤0.82 | 0.10–3.04 | 0.10–3.04 |
| | HT | 0.25 | 0.34–0.55 | 0.21–0.55 | ≤1.51 | ≤0.89 |
| | F | ≥0.14 | 0.21–1.30 | 0.14–0.62 | 0.29–5.21 | 0.29–1.97 |
| Mn | N | ≥0.001 | ≤0.08 | nr | ≤0.02 | ≤0.02 |
| | HT | 0 | nd | nd | ≤0.04 | ≤0.04 |
| | F | 0 | ≤0.15 | nd | nd | nd |
| Fe | N | ≥0.05 | ≤1.01 | ≤1.55 | 0.14–5.43 | 0.14–5.43 |
| | HT | 0.05 | nd | nd | ≤0.09 | ≤0.08 |
| | F | 0–0.4 | nd | ≤0.08 | ≤1.05 | ≤0.20 |
| Cl | N | nr | nd | nd | 0.01–0.19 | 0.01–0.19 |
| | HT | nr | 0.3–0.4 | ≤0.3 | 0.02–1.14 | 0.02–1.14 |
| | F | nr | nd | nd | 0.01–0.16 | 0.01–0.16 |

[a] Numbers in brackets are the numbers of stones in the categories. nr = not reported; nd = not detected.
[b] N, natural; HT, hydrothermal; F, flux.
[c] Excluding Taiwan flux, Russian flux and Russian hydrothermal samples.

The first reason is definitely valid for those elements with low concentrations. The discrepancy for Cl concentrations is explained by this factor. For example, Cl was not detected in all natural emeralds[3,4] in previous investigations, but was detected in all the hydrothermal stones,[4] which was believed to be due to the chloride hydrate ($CrCl_3 \cdot 6H_2O$) used to supply Cr as a coloring agent.[12] However, it was shown in our previous paper[13] that Cl is a brine component which is present in almost all emeralds, whether natural or synthetic.

To investigate the validity of the second reason, we analyzed the localities of the natural stones and the manufacturers of the synthetic stones used in the present work, the breakdown of which is shown in Table 7. As mentioned before, we had Taiwan flux, Russian flux and Russian hydrothermal emeralds which were not included in previous investigations.[1,3,4] Therefore, it is possible that these stones have elemental concentrations outside the range of

**Table 7. Analysis of the localities of the natural stones and the manufacturers of the synthetic stones used in this work (the Taiwan flux, Russian flux and Russian hydrothermal emeralds were not included in previous investigations)**

| This work | Schrader[1] | Hanni[3] | Stockton[4] |
|---|---|---|---|
| Colombian | √ (Chivor) | √ | √ |
| Pakistan | √ | √ | √ |
| Zambian | | √ | √ |
| Brazil | √ | √ | √ |
| Chatham flux | √ | √ | √ |
| Gilson flux | √ | √ | √ |
| Russian flux | | | |
| Taiwan flux | | | |
| Lennix flux | | √ | |
| Biron hydrothermal | | | √ |
| Russian hydrothermal | | | |
| Lechleitner | √ | √ | |

concentrations recorded in early investigations. Therefore, in the last column of Table 6, we also include for comparison the data excluding those of Taiwan flux, Russian flux and Russian hydrothermal emeralds. This greatly tightens the ranges for Cr in flux and hydrothermal grown stones and for V and Fe in flux grown stones.

To investigate the validity of the third reason, we compared the range of concentrations of Cr, Fe, V, Mn, Ni and Sc in different types of emeralds obtained in the present work and in Ref. 1 (see Table 8). Except for the difference for the Colombian stones, which might be explained by the different mines from which the stones came, i.e. Muzo mine for our stones and Chivor mine for Schrader's, the difference for other types of emeralds can only be explained if the properties of the stones vary significantly even for a single locality or manufacturer. Therefore, without a reasonably large sample of stones, the results and criteria should be treated with care. Further statistical analyses among elemental concentrations will be very useful, and will be presented in the following section.

## STATISTICAL ANALYSIS

This section is devoted to devising a scheme for emerald attribution by statistical analyses among elemental concentrations. In addition to looking at the natural and synthetic stones, we also include a category called 'Biron hydrothermal at the boundary', which refers to the scans over the boundary between the Biron hydrothermal grown emerald and the seed crystal.

### Correlation among chemical elements

The correlation among the three chromophoric elements Cr, V and Fe was studied through a 3D plot of the elemental concentrations. The reasons were twofold. First, it is known that different emeralds have different colors and tints. As the emerald color-causing transition elements are Cr, V and Fe,[14] and they have different efficiencies of coloration, it is expected that different emeralds have different distributions on the 3D plot. Second, from the PIXE spectra for emeralds in Fig. 1, the variations of the intensity peaks for these three elements and in particular the ratios between them were found to vary only slightly within a category but significantly across categories, which pointed to the feasibility of using these three elements for emerald attribution.

The result is shown in Figs 2 and 3. The two Taiwan flux emeralds had extraordinarily high Cr concentrations and were easily singled out. To spread out the other data for easy visualization, the data for these Taiwan flux emeralds were not included in the plot. Besides attributing the Taiwan flux emeralds, it was noticed from Fig. 2 that Pakistan emeralds and Chatham, Gilson and Lennix flux emeralds could be attributed. Although the Lechleitner emerald was separated from all other categories of emeralds, it was easily confused with the Biron hydrothermal emeralds so it could not be attributed. From Fig. 3, although the Colombian emeralds and the Biron hydrothermal emeralds (including those measured at the boundary) could be barely separated from each other, they were easily confused with each other, so again, they could not be attributed.

Therefore, in studying the correlation among the three chromophoric elements Cr, V and Fe, only the Pakistan emeralds and Chatham, Gilson, Taiwan and Lennix flux emeralds could be attributed. Apparently, to achieve the goal of being able to attribute emeralds of all different categories, more elemental concentrations should be employed. Principal component analysis will be used in this situation.

### Principal component analysis

The idea behind the principal component analysis (PCA) is to reduce the number of related variables to a smaller number of principal components (PCs) which are linear combinations of the previously mentioned related variables. By definition, the first principal component (PC1) has the largest variance, the second principal component (PC2) the second largest, and so on. Different categories of data will have different distributions of elemental concentrations and thus different values for the PCs. Therefore, 3D or 2D plots of PCs will enable us to separate visually different categories of data.

**Table 8. Comparisons of the range of concentrations of the elements Cr and Fe (%), V, Mn, Ni and Sc (ppm) in different types of emeralds obtained in this work and obtained by Schrader,[1] with zero referring to concentrations below the limits of detection[a]**

| Sample | Study[a] | Cr (%) | Fe (%) | V (ppm) | Mn (ppm) | Ni (ppm) | Sc (ppm) |
|---|---|---|---|---|---|---|---|
| Colombian | This work (20) | 0.10–1.69 | 0.14–1.90 | 300–8535 | 0–124 | 0–50 | 205–1436 |
| | Schrader (10) | ≥0.10 | 0.05–0.35 | ≥130 | 10–26 | 0–50 | 0–1100 |
| Pakistan | This work (6) | 1.18–3.04 | 0.97–5.09 | 367–1692 | 0–0 | 16–98 | 2075–7951 |
| | Schrader (2) | 0.13–0.14 | 0.48 | ≥500 | 10–15 | 70–130 | 1000–1700 |
| Brazil | This work (5) | 0.54–1.62 | 3.88–5.21 | 1208–1822 | 0–189 | 62–133 | 339–2934 |
| | Schrader (16) | 0–0.45 | ≥0.19 | ≥50 | ≥15 | 0–50 | 0–200 |
| Chatham Flux | This work (5) | 1.55–1.97 | 0.01–0.02 | 0–0 | 0–0 | 0–0 | 0–0 |
| | Schrader (5) | ≥0.35 | ~0 | 0 | <2 | ≤10 | 0 |
| Gilson Flux | This work (4) | 0.81–1.75 | 0.10–0.20 | 32–2176 | 0–0 | 23–72 | 0–0 |
| | Schrader (6) | ≥0.14 | 0.02–0.20 | 0–430 | <2 | 0–30 | 0 |
| Lechleitner | This work (1) | 0 | 0.03 | 0 | 356 | 10 | 49 |
| | Schrader (1) | 0.25 | 0.05 | 0 | <2 | 0 | 0 |

[a] The numbers in brackets are the number of samples in the category.

 

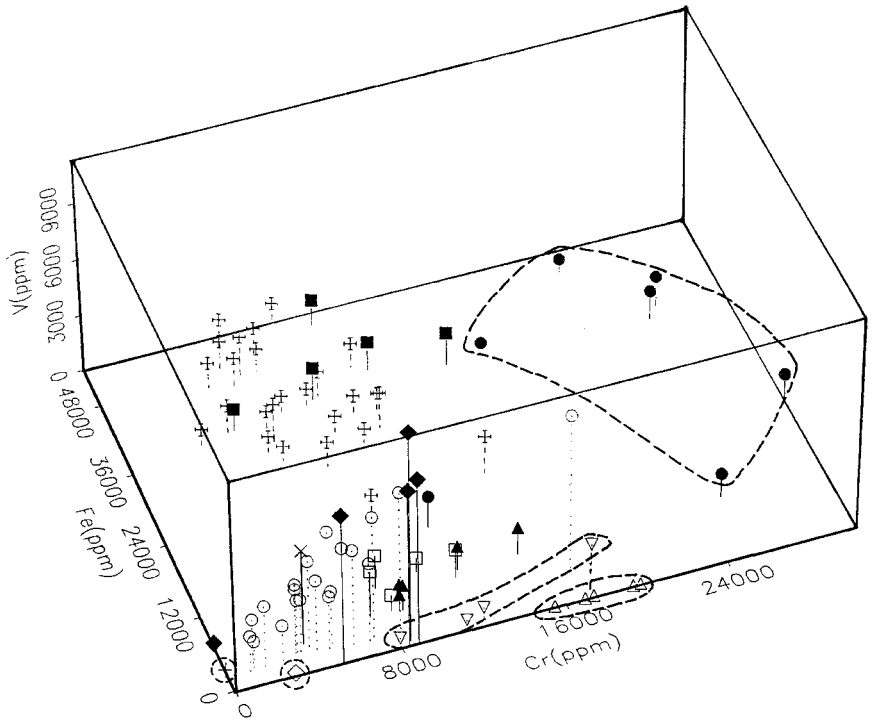


**Figure 2.** Three-dimensional plot to show the correlation among the concentrations of the three chemical elements, Cr, Fe and V for all the emerald data. ○, Colombia; ●, Pakistan; ✠, Zambian; ■, Brazil; △, Chatham flux; ▽, Gilson flux; □, Russian flux; ◊, Lennix flux; ◆, Biron hydrothermal; ×, Biron hydrothermal at the boundary; ▲, Russian hydrothermal; +, Lechleitner. The two Taiwan flux emeralds have extraordinarily high Cr concentrations and are easily singled out. To spread out the other data, the data for these Taiwan flux emeralds have not been included.

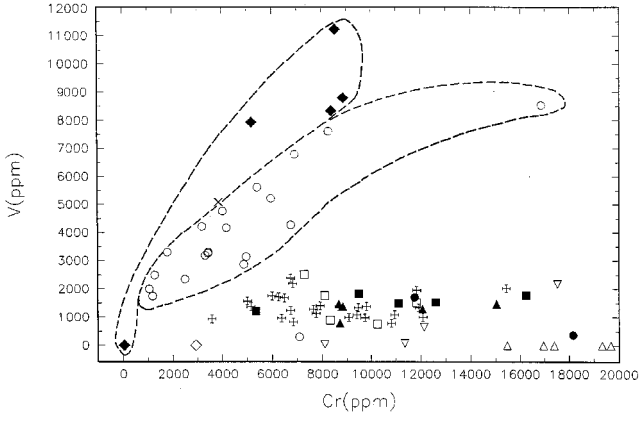


**Figure 3.** Plot of the concentration of V against that of Cr for all the emerald data. Symbols as in Fig. 2.

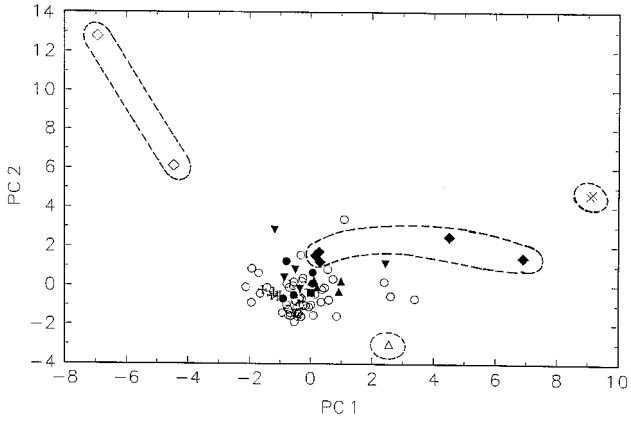


**Figure 4.** Plot of the second principal component (PC2) against the first principal component (PC1) for all the emerald data. ○, Natural emeralds; ✠, Chatham flux; ▲, Gilson flux; ▼, Russian flux; ◊, Taiwan flux; ■, Lennix flux; ◆, Biron hydrothermal; ×, Biron hydrothermal at the boundary; ●, Russian hydrothermal; △, Lechleitner.

The concentrations of all 32 elements quantitatively measured for the emeralds by PIXE were analyzed by PCA using SAS software (version 6.04) (SAS Institute, Cary, NC, USA). The results are shown in Figs 4–7, in which PC2 and PC3 are plotted against PC1 for all emerald data. Data for natural emeralds are grouped together as a single category in Figs 4 and 5, whereas data for synthetic emeralds are grouped together as a single category in Figs 6 and 7. From Fig. 4 (PC2 vs PC1), the Taiwan flux emeralds, Biron hydrothermal emeralds and those measured at the boundary, and the Lechleitner emeralds can be separated out. From Fig. 5 (PC3 vs PC1), the Chatham flux, Gilson flux and Lennix flux emeralds can further be separated out. However, the remaining data for Russian flux and Russian hydrothermal emeralds are still entangled with each other. In Figs 6 and 7 (PC2 and PC3 vs PC1, respectively), the data for natural emeralds are entangled.

The tangles of the data might arise from the procedure whereby we analyzed the data for natural and synthetic emeralds together. These two categories of data might have very different properties and thus different correlations among concentrations of chemical elements within each category. Therefore, the simultaneous PCA of the two categories of data will not efficiently separate out individual groups of data. Very fortunately, from Figs 4 and 5, natural and synthetic emeralds can be separated

 

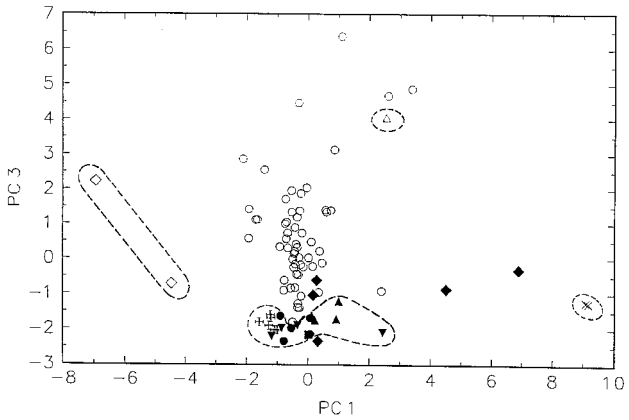


**Figure 5.** Plot of the third principal component (PC3) against the first principal component (PC1) for all the emerald data. Symbols as in Fig. 4.

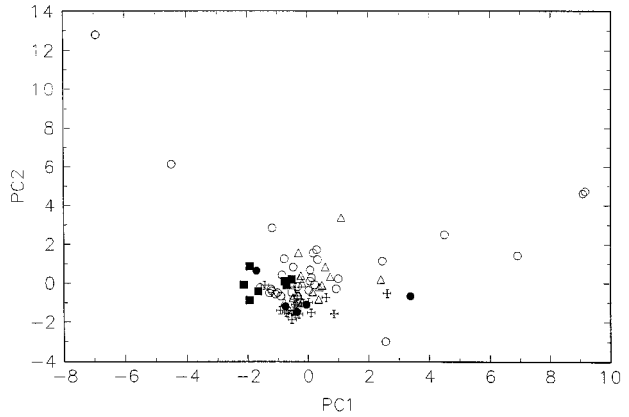


**Figure 6.** Plot of the second principal component (PC2) against the first principal component (PC1) for all the emerald data. ○, Synthetic emeralds; △, Colombia; ■, Pakistan; ✠, Zambia; ●, Brazil.

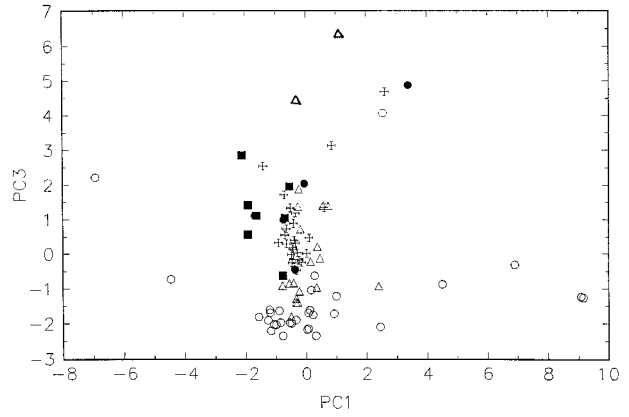


**Figure 7.** Plot of the third principal component (PC3) against the first principal component (PC1) for all the emerald data. Symbols as in Fig. 6.

from each other, so that we can look at one category at a time.

In Figs 8 and 9, PC2 and PC3 are plotted against PC1 for natural emerald data. From Fig. 8, emeralds from Colombia and Zambia are comfortably separated. It seems that there are tangles between the emeralds from Pakistan and Brazil for PC1 values smaller than −0.5. However,

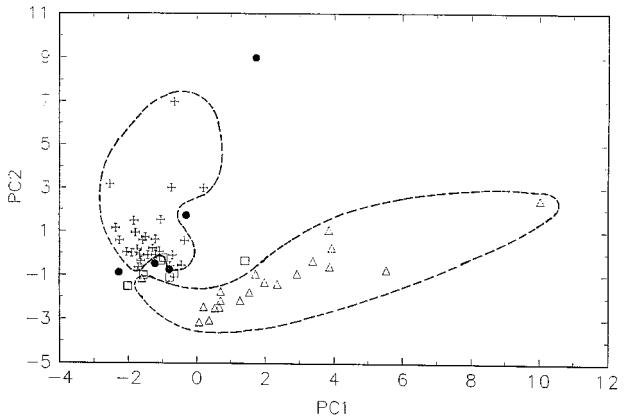


**Figure 8.** Plot of the second principal component (PC2) against the first principal component (PC1) for the natural emerald data. △, Colombia; □, Pakistan; ✠, Zambia; ●, Brazil.

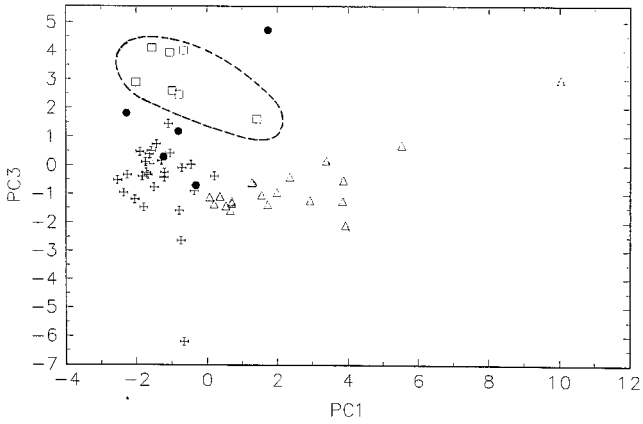


**Figure 9.** Plot of the third principal component (PC3) against the first principal component (PC1) for the natural emerald data. Symbols as in Fig. 8.

from Fig. 9, all Pakistan emeralds have larger PC3 values than Brazilian stones here. Therefore, the emeralds from the two localities in fact occupy distinct zones in the three-dimensional (PC1–PC2–PC3) space, and are thus also separated out. In this way, all the localities of natural emeralds studied in the present investigation can be attributed using PCA.

In Fig. 10, PC2 is plotted against PC1 for synthetic emerald data. The data for Taiwan flux emeralds and the Biron hydrothermal emerald measured at the boundary are clearly separated out. For better visualization of the data, the data for Taiwan flux emeralds are not included in Fig. 11 in which PC3 is plotted against PC1 for synthetic emerald data. From Fig. 11, all types of synthetic emeralds can be satisfactorily separated except that there are tangles between the Russian flux and Russian hydrothermal emeralds.

Therefore, through the PCA of the concentrations of all the 32 elements quantitatively measured for the emeralds by PIXE, the emerald attributions are successful except that the Russian flux and Russian hydrothermal emeralds cannot be separated. The coefficients for the concentrations of elements in the first three PCs are shown in Table 9. In future real-life testing, the concentrations of elements in an emerald of an unknown origin can be determined by PIXE, which are then substituted into

 

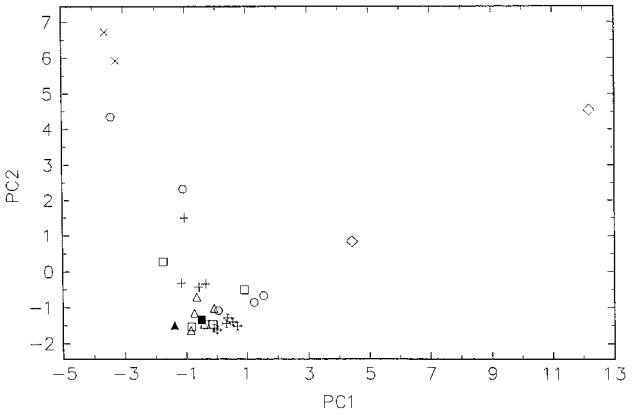


**Figure 10.** Plot of the second principal component (PC2) against the first principal component (PC1) for the synthetic emerald data. ✠, Chatham flux; +, Gilson flux; □, Russian flux; ◊, Taiwan flux; ■, Lennix flux; O, Biron hydrothermal; ×, Biron hydrothermal at the boundary; △, Russian hydrothermal; ▲, Lechleitner.

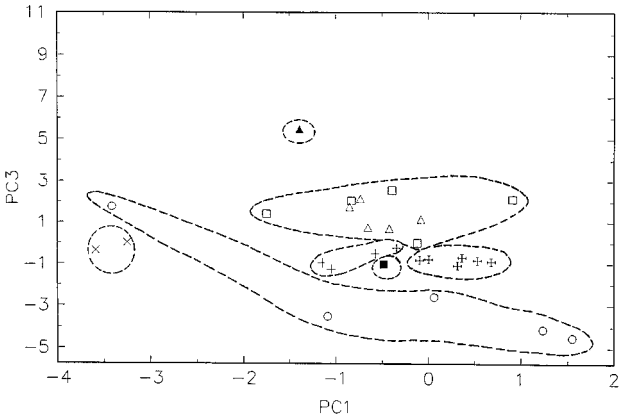


**Figure 11.** Plot of the third principal component (PC3) against the first principal component (PC1) for all the emerald data. For better visualisation of the data, the data for Taiwan flux emeralds have not been included. Symbol as those in Fig. 10.

appropriate PCs using these coefficients to decide its position on the principal component plots, from which a final attribution can be made.

After the successful emerald attributions using the concentrations of 32 elements, we had a more aggressive objective, i.e. to use a reduced set of elements for emerald attribution. In normal investigations of emerald properties, fewer elements are studied. Therefore, if we can accomplish this objective, this method would be much more useful and convenient. We choose the six elements which were also measured in previous investigations of emeralds,[1,3,4] i.e. Cr, Fe, V, Mn, Ti and Cl for the PCA using the SAS software. The results are shown

**Table 9. Coefficients for the concentrations of chemical elements in the first three principal components (PCs) when all 32 chemical elements are considered**

| | All emeralds | | | Natural emeralds | | | Synthetic emeralds | | |
|---|---|---|---|---|---|---|---|---|---|
| Element | PC1 | PC2 | PC3 | PC1 | PC2 | PC3 | PC1 | PC2 | PC3 |
| P | −0.206 | 0.353 | −0.048 | −0.137 | 0.022 | 0.026 | 0.307 | 0.082 | 0.100 |
| S | 0.112 | 0.025 | 0.167 | 0.013 | 0.252 | −0.252 | −0.032 | 0.193 | −0.008 |
| Cl | 0.232 | 0.165 | −0.090 | 0.348 | 0.037 | −0.095 | −0.056 | 0.150 | −0.320 |
| K | 0.394 | 0.133 | −0.002 | 0.162 | 0.268 | 0.061 | −0.199 | 0.319 | 0.059 |
| Ca | 0.191 | 0.011 | 0.288 | 0.069 | 0.323 | −0.017 | −0.116 | 0.319 | −0.031 |
| Sc | −0.106 | −0.100 | 0.229 | −0.119 | 0.004 | 0.290 | −0.023 | −0.119 | 0.245 |
| Ti | 0.342 | 0.133 | −0.016 | 0.003 | 0.195 | 0.246 | −0.168 | 0.360 | −0.015 |
| V | 0.099 | 0.238 | 0.104 | 0.372 | −0.079 | −0.044 | 0.078 | 0.169 | −0.256 |
| Cr | −0.242 | 0.218 | 0.045 | −0.074 | 0.050 | 0.414 | 0.267 | 0.002 | −0.011 |
| Mn | 0.104 | −0.087 | 0.265 | 0.068 | 0.285 | −0.073 | −0.035 | −0.051 | 0.235 |
| Fe | −0.056 | −0.202 | 0.258 | −0.299 | 0.264 | 0.100 | −0.126 | −0.001 | 0.318 |
| Co | −0.035 | −0.040 | 0.176 | 0.012 | 0.047 | 0.058 | −0.053 | 0.064 | 0.020 |
| Ni | −0.023 | −0.018 | −0.131 | −0.189 | 0.217 | −0.053 | −0.056 | −0.125 | 0.255 |
| Cu | 0.270 | 0.115 | 0.046 | 0.316 | 0.120 | 0.027 | −0.169 | 0.215 | 0.025 |
| Zn | 0.368 | 0.094 | −0.012 | 0.137 | 0.310 | −0.179 | −0.196 | 0.244 | 0.191 |
| Ga | 0.035 | −0.146 | 0.222 | 0.058 | 0.062 | −0.378 | −0.088 | 0.170 | 0.301 |
| As | −0.201 | 0.373 | 0.041 | 0.085 | 0.147 | 0.114 | 0.320 | 0.136 | 0.097 |
| Br | −0.202 | 0.313 | 0.039 | −0.060 | −0.025 | 0.124 | 0.320 | 0.116 | 0.120 |
| Rb | 0.058 | −0.087 | 0.139 | −0.051 | 0.198 | 0.225 | −0.050 | −0.076 | 0.302 |
| Sr | 0.035 | 0.088 | 0.013 | −0.073 | −0.021 | 0.065 | −0.036 | 0.224 | −0.013 |
| Y | −0.045 | 0.027 | 0.016 | −0.018 | −0.013 | −0.076 | 0.307 | 0.155 | 0.092 |
| Zr | −0.153 | 0.259 | 0.110 | −0.065 | 0.098 | −0.020 | 0.307 | 0.155 | 0.092 |
| Mo | −0.005 | −0.004 | −0.088 | 0.000 | 0.000 | 0.000 | −0.016 | 0.004 | −0.085 |
| Cs | 0.067 | −0.166 | 0.260 | −0.199 | 0.277 | 0.178 | −0.061 | −0.010 | 0.284 |
| Ba | −0.080 | 0.135 | 0.325 | 0.237 | −0.005 | 0.265 | 0.255 | 0.126 | −0.139 |
| La | −0.031 | 0.102 | 0.446 | 0.282 | 0.161 | 0.219 | 0.200 | 0.024 | 0.034 |
| Ce | −0.050 | 0.200 | 0.326 | 0.341 | 0.087 | 0.128 | 0.318 | 0.130 | 0.112 |
| W | 0.060 | 0.004 | 0.155 | 0.061 | 0.178 | −0.245 | 0.051 | −0.037 | −0.266 |
| Pt | 0.197 | 0.302 | 0.043 | −0.042 | 0.212 | −0.173 | 0.037 | 0.363 | 0.036 |
| Au | 0.315 | 0.183 | −0.049 | 0.158 | 0.207 | 0.167 | −0.119 | 0.313 | −0.010 |
| Pb | −0.097 | 0.214 | −0.089 | −0.188 | 0.242 | −0.186 | 0.138 | 0.018 | 0.177 |
| Bi | −0.035 | −0.136 | 0.143 | −0.196 | 0.190 | 0.005 | −0.005 | −0.013 | −0.227 |

 

in Figs 12–15, in which PC2 and PC3 are plotted against PC1 for all emerald data. Data for natural emeralds are grouped together as a single category in Figs 12 and 13, while data for synthetic emeralds are grouped together as a single category in Figs 14 and 15. From Figs 12 and 13, the Taiwan flux emeralds, Biron hydrothermal emeralds and those measured at the boundary, and the Lechleitner emeralds can be attributed. The other synthetic emeralds are all entangled with each other. From Figs 14 and 15, only Pakistan stones can be attributed because they occupy a distinct region in the 3D PC1–PC2–PC3 space. The emeralds from the other three localities are entangled with each other. A major drawback here is that the synthetic emeralds being entangled in Figs 12 and 13 (i.e. the Chatham, Gilson, Russian and Lennix flux emeralds and Russian hydrothermal emeralds) are also entangled with the unresolved natural stones, so no further separate analyses of natural and synthetic emeralds can be performed. Therefore, PCA of six elements only allowed us to attribute the Pakistan emeralds, Taiwan flux emeralds, Biron hydrothermal emeralds and Biron hydrothermal emeralds measured at the boundary, and Lechleitner emeralds. The coefficients for the concentrations of these six chemical elements in the first three PCs are shown in Table 10.

## CONCLUSIONS

A total of 56 natural emeralds and 26 synthetic emeralds were studied by PIXE. For natural emeralds, we had 20 from Colombia, six from Pakistan, 25 from Zambia and five from Brazil. For synthetic emeralds, we had five Chatham, four Gilson, five Russian, two Taiwan and one Lennix stones which were manufactured using the flux method, and three Biron, five Russian and one Lechleitner stones which were manufactured using the hydrothermal method. The Taiwan flux, Russian flux and Russian hydrothermal emeralds were not included in previous investigations. From the PIXE spectra and the concentrations of 33 elements, i.e. Sc, Ti, V, Cr, Mn, Fe, Ni, K, Rb, Cs, Ca, Sr, Ba, Co, Cu, Zn, Y, Zr, La, Ce, Ga, P, S, Cl, As, Br, Mo, W, Pb, Bi, Pt, Au and Rh, obtained from the bulk analyses of inclusion-free regions of the stones, criteria for differentiating between natural and synthetic emeralds and among different localities of natural emeralds were deduced. It was also concluded that the properties of emeralds vary significantly even for a single locality or manufacturer.

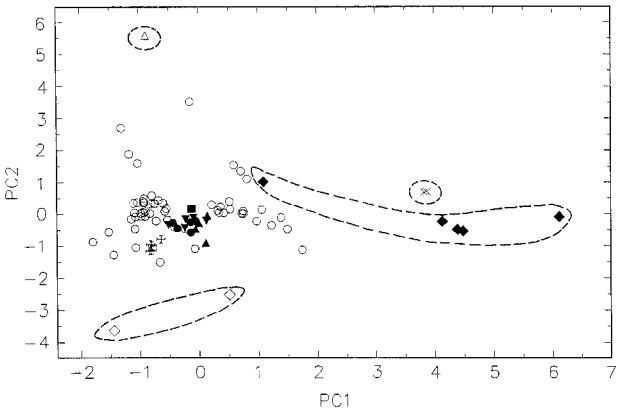


**Figure 12.** Plot of the second principal component (PC2) against the first principal component (PC1) from PCA of six selected chemical elements for all the emerald samples. ○, Natural emeralds; ✠, Chatham flux; ▲, Gilson flux; ▼, Russian flux; ◊, Taiwan flux; ■, Lennix flux; ◆, Biron hydrothermal; ×, Biron hydrothermal at the boundary; ●, Russian hydrothermal; △, Lechleitner.

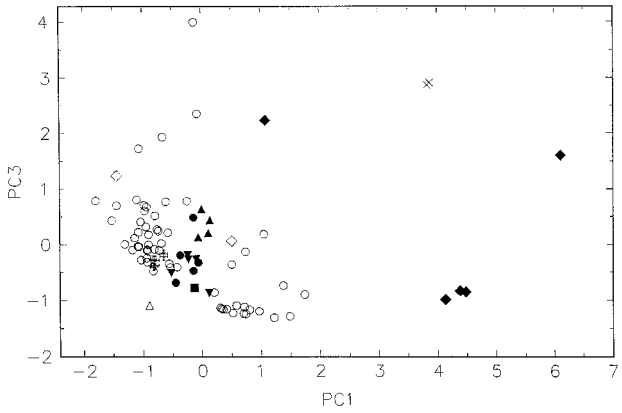


**Figure 13.** Plot of the third principal component (PC3) against the first principal component (PC1) from PCA of six selected chemical elements for all the emerald samples. Symbols as in Fig. 12.

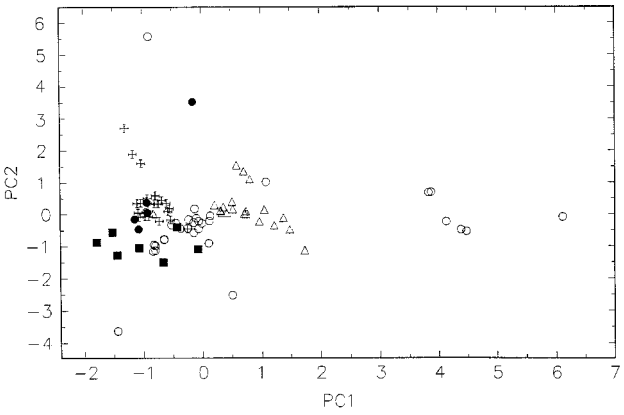


**Figure 14.** Plot of the second principal component (PC2) against the first principal component (PC1) from PCA of six selected chemical elements for all the emerald samples. ○, Synthetic emeralds; △, Colombia; ■, Pakistan; ✠, Zambia; ●, Brazil.

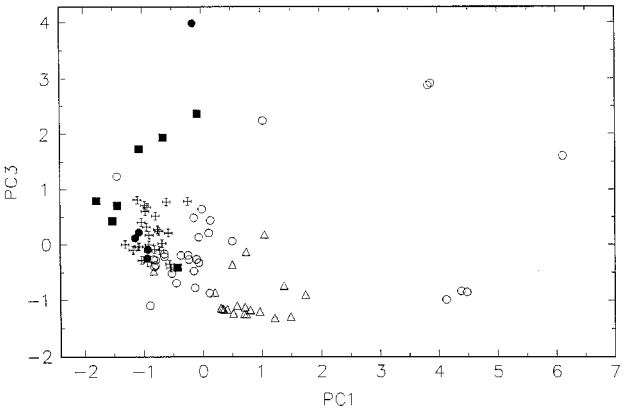


**Figure 15.** Plot of the third principal component (PC3) against the first principal component (PC1) from PCA of six selected chemical elements for all the emerald samples. Symbols as in Fig. 14.

**Table 10. Coefficients for the concentrations of chemical elements in the first three principal components (PCs) when six elements are considered**

| Element | PC1 | PC2 | PC3 |
|---|---|---|---|
| Cl | 0.623 | 0.010 | 0.128 |
| Ti | 0.275 | 0.154 | 0.839 |
| V | 0.589 | −0.067 | −0.183 |
| Cr | −0.194 | −0.623 | 0.348 |
| Mn | −0.062 | 0.732 | −0.005 |
| Fe | −0.385 | 0.220 | 0.353 |

Schemes for unambiguous emerald attribution (to a specific locality or type) were also devised from its elemental concentrations. This was started by studying the correlation among the three chromophoric elements Cr, V and Fe through a 3D plot of elemental concentrations. The Pakistan emeralds and Chatham, Gilson, Taiwan and Lennix flux emeralds could be attributed. Apparently, this was only a partial success. In order to achieve the goal of being able to attributing all different categories of emeralds, more elemental concentrations should be used, in which principal component analysis (PCA) should be employed.

Through PCA of the concentrations of 32 elements, emeralds of different categories studied in this project could all be attributed except that the Russian flux and hydrothermal emeralds could not be separated from each other. Therefore, the attributed categories included the natural emeralds from Colombia, Pakistan, Zambia and Brazil, flux grown synthetic emeralds from Chatham, Gilson, Taiwan and Lennix, hydrothermal grown synthetic emeralds from Biron and Lechleitner, and a mixed group incorporating Russian flux and Russian hydrothermal emeralds. Coefficients for the concentrations of the chemical elements in the first three PCs from the PCA of all emerald data, natural emerald data alone and synthetic emerald data alone were given, which can be used in future real-life tests of unknown emeralds. Looking back at Figs 2 and 3, the study of the correlation among the three chromophoric elements Cr, V and Fe through a 3D plot of the elemental concentrations also attributed this mixed group.

According to the basic principle of PCA, there is a relatively small difference in the characteristics between the Russian flux and Russian hydrothermal emeralds. In fact, it was found previously[13] that the inclusions in Russian hydrothermal emeralds resembled those of Russian flux emeralds, viz. both of them exhibited the characteristic veil-like flux inclusions correlating Pb, V and S. The existence of these features in hydrothermal stones was surprising because Pb was thought to be a flux component and it was noticed that Pb was not identified in other hydrothermal grown emeralds studied in this project, i.e. the Biron and Lechleitner emeralds. The PIXE spectra for the Russian flux and Russian hydrothermal emeralds were also found to be very similar in previous sections. The close resemblance between the two types of synthetic stones is not yet understood.

A more aggressive objective was then to use a reduced set of elements, i.e. Cr, Fe, V, Mn, Ti and Cl, for emerald attribution. PCA of these six elements allowed us to attribute the Pakistan emeralds, Taiwan flux emeralds, Biron hydrothermal emeralds and Biron hydrothermal emeralds measured at the boundary, and Lechleitner emeralds. Again, coefficients for the concentrations of chemical elements in the first three PCs from the PCA of these six elements were given, which can be used in future routine tests of unknown emeralds. Although the PCA did not attribute emeralds of all categories, this can be combined with the study of correlation among the three chromophoric elements Cr, V and Fe through a 3D plot of the elemental concentrations to attribute all synthetic emeralds (including a mixed group incorporating the Russian flux and Russian hydrothermal emeralds), the Colombian and Pakistan emeralds. This will be useful and convenient in separating natural from synthetic emeralds and in attributing synthetic emeralds.

## Acknowledgement

K. N. Yu acknowledges the hospitality of the Department of Physics of the National University of Singapore during his stay.

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